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Rate coefficients of open shell molecules and radicals: *R*-matrix method

JASMEET SINGH[1,2], K L BALUJA[1] and GAGANDEEP LONGIANY[1,2,*]

[1]Department of Physics and Astrophysics, University of Delhi, Delhi 110 007, India
[2]Keshav Mahavidyalaya, Department of Physics, University of Delhi, Delhi 110 034, India
*Corresponding author. E-mail: gagandeep.longiany@gmail.com

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Abstract. The open shell molecules with even number of electrons have π^2 or π_g^2 ground-state electronic configuration. Several homonuclear diatomic molecules like O_2, S_2, B_2 have π_g^2 ground state in the $D_{\infty h}$ point group and heteronuclear diatomic radicals like PH, NH, SO have π^2 ground state in the $C_{\infty v}$ point group. We have computed and presented here the rate coefficient of these open shell molecules (O_2, S_2, B_2) and radicals (PH, NH, SO) from the results of our previous studies using a well-established *ab-initio* formalism: the *R*-matrix method. The rate coefficients for elastic and electron-excited processes are studied over a wide electron temperature range.

Keywords. Molecular processes; rate coefficients.

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1. Introduction

Electron–molecule collisions give rise to various processes like electronic, vibrational and rotational excitations. These excitations are involved in many applications in different fields like plasma processing, lasers, study of structure of DNA and astrophysics which require a large amount of data on molecular processes. The required information can be computed by quantum mechanical calculations using the *R*-matrix method. Because of the large amount of information required for plasma modelling, interstellar atmosphere research and astrophysical applications, only theory can provide the bulk of the input data comprising mainly the excitation rate coefficients along with the energy level structure and transition probabilities which are not experimentally known. These requirements and study related to the molecules which have astrophysical importance provoke the need of computation of rate coefficients for elastic and electron-excited processes.

Many molecules with even number of electrons belong to open shell system due to π^2 or π_g^2 ground-state electronic configuration. This configuration gives rise to three low-lying states $X^3\Sigma_g^-$, $a^1\Delta_g$ and $b^1\Sigma_g^+$ in homonuclear diatomic molecules (O_2, S_2, B_2) and $X^3\Sigma^-$, $a^1\Delta$ and $b^1\Sigma^+$ in heteronuclear diatomic radicals (PH, NH, SO).

The *R*-matrix method is a well-established *ab-initio* formalism to calculate elastic and inelastic scattering of electrons by molecules. We have calculated these cross-sections in our previous study [1–3]. The present study uses the results of *ab-initio* *R*-matrix method to low-energy scattering of the open shell molecules in the fixed nuclei approximation to compute rate coefficients. The rate coefficients for elastic and electron-excited processes are studied over a wide electron temperature range. The calculations use the UK molecular *R*-matrix code [4,5]. After a comprehensive study and modernization in coding, the suite is now called UKRmol [6–8].

2. Method

Since the *R*-matrix theory has been described in detail elsewhere [9–12], only a brief summary is given in this section. The basic idea of the *R*-matrix method is the partition of configuration space into inner and outer regions, separated by a sphere of radius a. The electron density of the target states is contained within the inner region. Exchange and correlation between

all electrons are in this region. The inner region wave function (eigenfunction of the total Hamiltonian) is

$$\psi_k^{N+1} = A \sum_{ij} a_{ijk} \phi_i^N (x_1, ..., x_N) u_{ij}(x_{N+1}) + \sum_i b_{ik} \chi_i^{N+1}(x_1, ..., x_{N+1}), \quad (1)$$

where the target contains N electrons and functions are labelled as N or $N+1$ according to whether they refer to the target or the composite scattering system respectively.

ϕ_i^N is the wave function of the ith target state and u_{ij} are the extra orbitals introduced to represent the scattering electron. The precise choice of the continuum orbitals, u_{ij}, is labelled by the target state index i as it depends on the symmetry of the particular target state. The function ϕ_i^N and u_{ij} must couple together to give the correct overall spatial and spin symmetry of the total wave function ψ_k^{N+1}. Furthermore, the electrons, whose space-spin coordinates are represented by x_i, must obey the Pauli principle and are therefore antisymmetrized by operator A.

The second summation in eq. (1) involves configurations which have no amplitude on the R-matrix boundary and where all electrons are placed in orbitals associated with the target. As they are confined to a finite volume of space, they will be referred to as L^2 configurations below. These (x_i) are bound-state wave functions of the $(N+1)$ electron system. The continuum orbitals are generated by orthogonalizing to the target molecular orbitals a set of Gaussian Tye Orbitals (GTOs) centred on the centre of mass of the system. The use of GTOs to describe the continuum simplifies the integral calculation. In more sophisticated models, the L^2 configurations are also used to model the effects of target polarization.

The coefficients a_{ijk} and b_{ik} are obtained by diagonalizing the matrix

$$\langle \psi_k^{N+1} | \mathbf{H} + \mathbf{L} | \psi_{k'}^{N+1} \rangle = \delta_{kk'} E_k, \quad (2)$$

where $\mathbf{H}$ is the Hamiltonian of a system of $(N+1)$-electrons and $\mathbf{L}$ is the Bloch operator [10]. Using the inner region wavefunctions and their associated eigenvalues, together with information on the target molecule to define channels, the R-matrix is built at the boundary between the two regions:

$$R_{ij}(E) = \frac{1}{2a} \sum_k \frac{w_{ik}(a) w_{jk}(a)}{(E_k - E)}, \quad (3)$$

where E_k, known as R-matrix poles, are the eigenvalues from eq. (2) and w_{ik} are

$$w_{ik}(a) = \langle \phi_i^N Y_{l_i,m_i} \Xi_{1/2} | \psi_k^{N+1} \rangle, \quad (4)$$

where ψ_k^{N+1} is the wave function of the kth R-matrix pole, see eq. (1), and ϕ_i^N is the target wave function for channel i. The integral runs over all space-spin coordinates except the radial coordinate of the scattering electron. The product $\phi_i^N Y_{l_i,m_i} \Xi_{1/2}$ defines the channels. The function $\Xi_{1/2}$ is a one-half electron spin function and Y_{l_i,m_i} are spherical harmonics.

In the outer region, exchange and correlation can be neglected and a single-centre multipole expansion exists. This leads to a set of coupled differential equations for the functions describing the radial behaviour of the projectile. The set of differential equations is solved by propagating the R-matrix from the boundary to some large radial distance beyond which the non-Coulombic potential can be neglected. The radial wave functions are then matched to asymptotic solutions of known form and K-matrices are obtained. The partial wave expansion is determined by the set of values chosen for l and m of the spherical harmonics describing the angular part of the continuum GTOs. The convergence of this expansion is rapid for most cases; including a few partial waves ($l \leq 4$). However, we have to use the dipole Born approximation, in the case of polar target having permanent dipole moment, to account for higher partial waves. In the multipole expansion, the transition moments are calculated from the wave functions of the target states, in the initial step of computation. For this, we have to define a model for the description of the target. That means, a basis set must be defined for the molecular orbitals, procedure for generating them and a configuration interaction (CI) model to generate the wave functions. We have used standard quantum chemistry basis sets [13]. We run a Hartree–Fock self-consistent field calculation (HF-SCF) to produce the orbitals. The static-exchange and static-exchange plus polarization scattering models employ a single configuration wave function to describe the ground state of the target. The CI model is used to describe various electronic states of the target using a single orbital set. Our theoretical results include accurate transition moments, excitation energies, dipole and quadrupole moments; implying the high-quality target wave functions generated in close-coupling calculations.

The elastic and inelastic cross-sections are used to obtain rate coefficients, which are defined as

$$K_i = \left(\frac{8}{m_e \pi}\right)^{1/2} \left(\frac{1}{k_B T_e}\right)^{3/2} \times \int_0^\infty E Q^i(E) \exp\left(-\frac{E}{k_B T_e}\right) \mathrm{d}E, \quad (5)$$

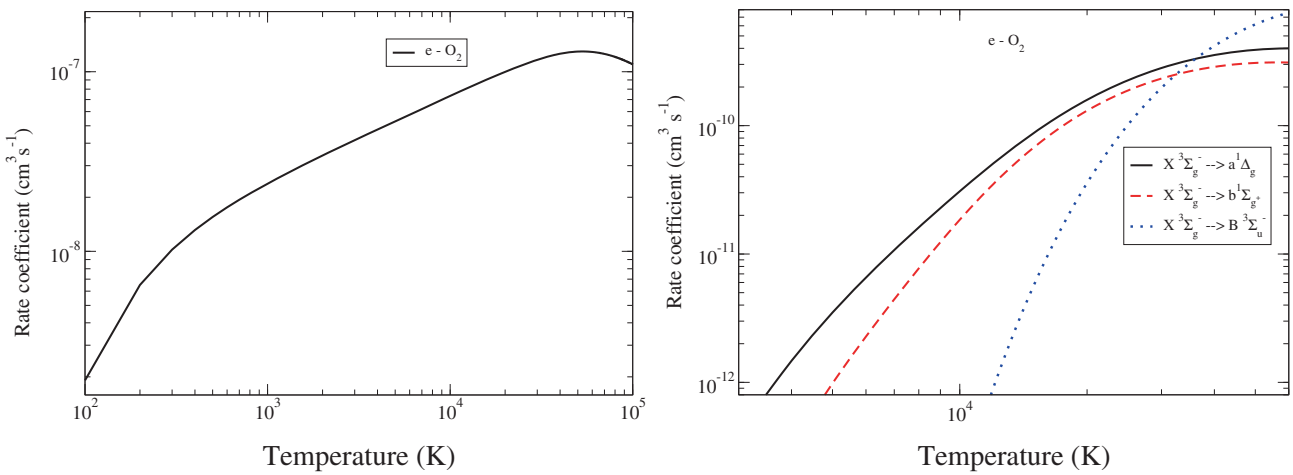

Figure 1. (**a**) Elastic rate coefficients of the O_2 molecule using SE model at bond length $R_e = 2.2a_0$ and (**b**) inelastic rate coefficients of the O_2 molecule using the 22-state CI model at bond length $R_e = 2.42a_0$ for various excited states.

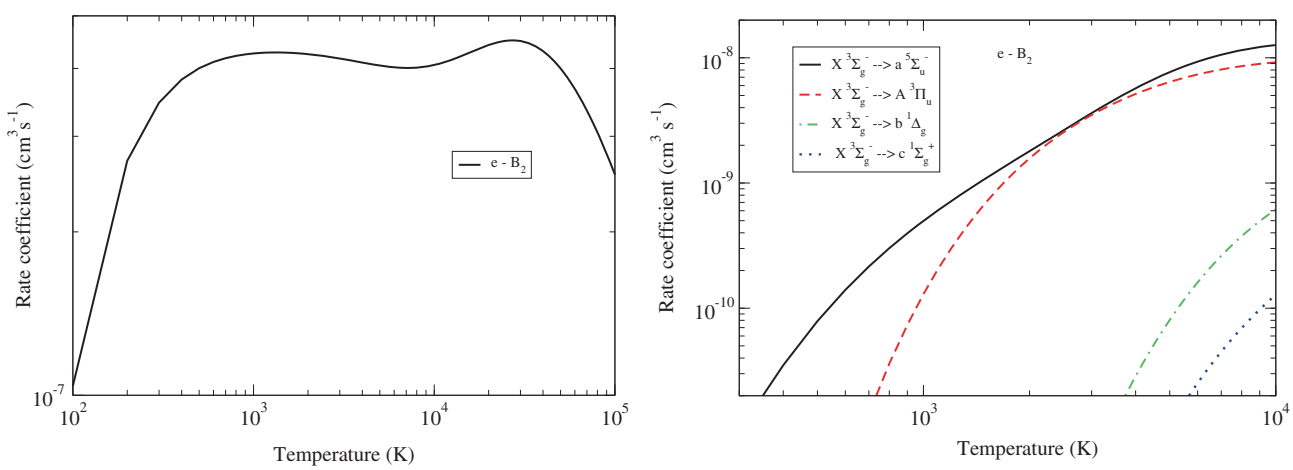

Figure 2. (**a**) Elastic rate coefficients of the B_2 molecule using SE model at bond length $R_e = 3.10a_0$ and (**b**) inelastic rate coefficients of the B_2 molecule using the 61-state CI model at bond length $R_e = 3.18a_0$ for various excited states.

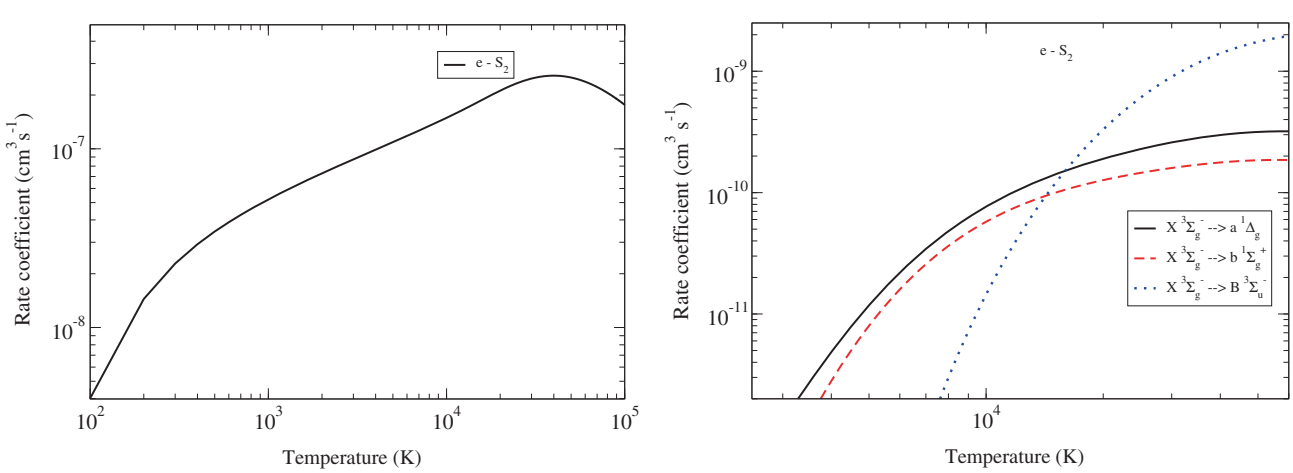

Figure 3. (**a**) Elastic rate coefficients of the S_2 molecule using SE model at bond length $R_e = 3.538a_0$ and (**b**) inelastic rate coefficients of the S_2 molecule using the 20-state CI model at bond length $R_e = 3.676a_0$ for various excited states.

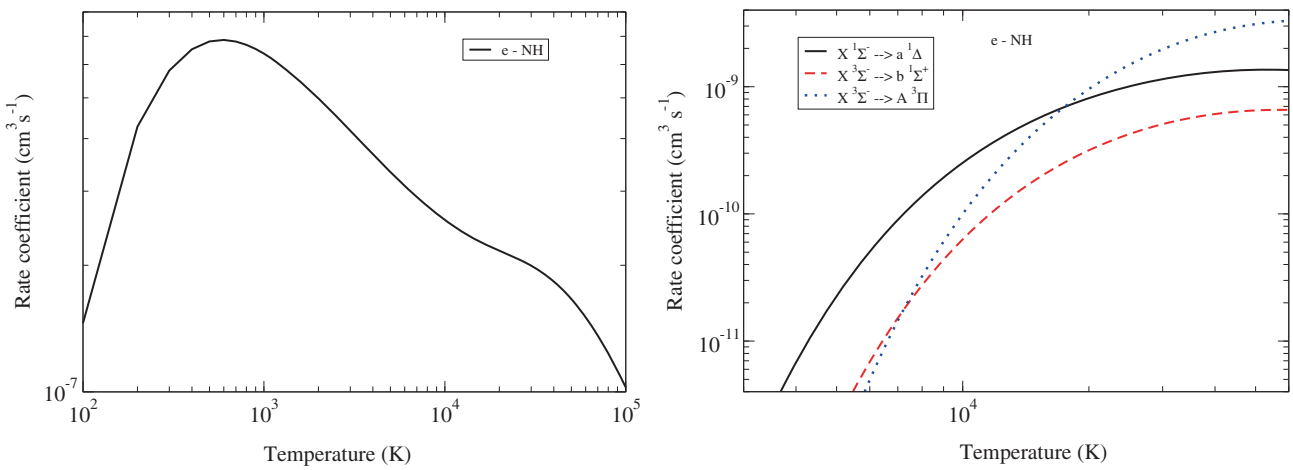

Figure 4. (**a**) Elastic rate coefficients of the NH radical using SE model at bond length $R_e = 1.94a_0$ and (**b**) inelastic rate coefficients of the NH radical using the 19-state CI model at bond length $R_e = 2.0a_0$ for various excited states.

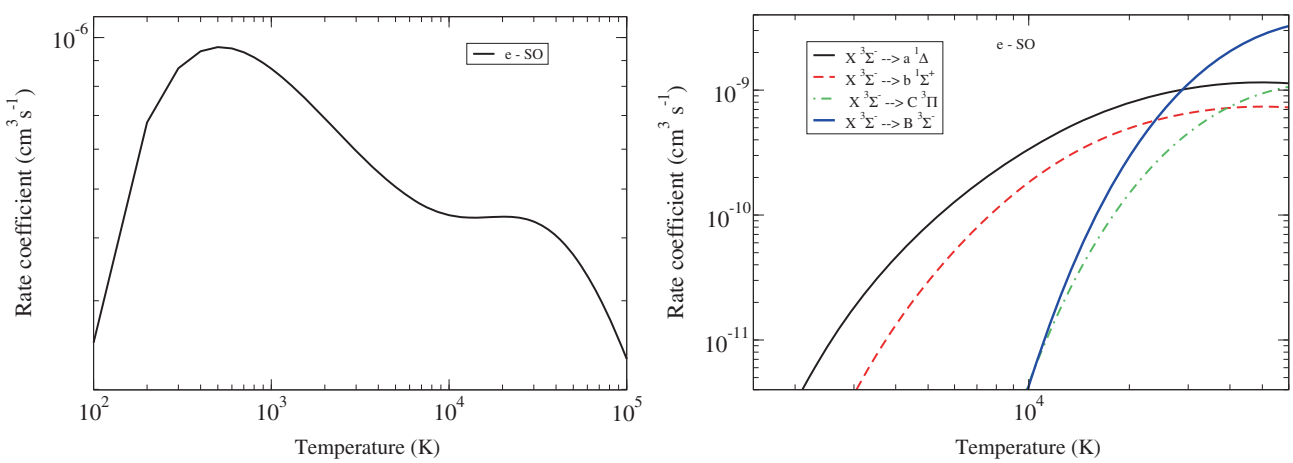

Figure 5. (**a**) Elastic rate coefficients of the SO radical using SE model at bond length $R_e = 2.77a_0$ and (**b**) inelastic rate coefficients of the SO radical using the 28-state CI model at bond length $R_e = 2.90a_0$ for various excited states.

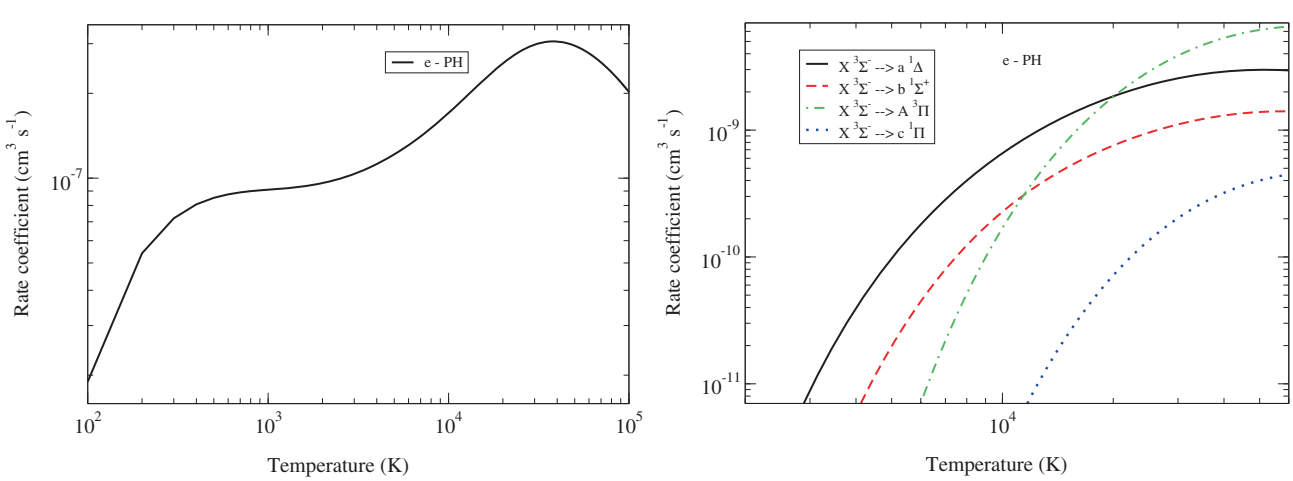

Figure 6. (**a**) Elastic rate coefficients of the PH radical using SE model at bond length $R_e = 2.687a_0$ and (**b**) inelastic rate coefficients of the PH radical using the 37-state CI model at bond length $R_e = 2.687a_0$ for various excited states.

where the cross-section $Q^i(E) = 0$ up to the threshold. For the elastic scattering cross-sections $i = 0$, and it is 1, 2, 3, 4 for cross-sections of several excited states. The rate coefficients for elastic and inelastic processes are computed over a wide electron temperature range.

3. Results

3.1 *Rate coefficients in SE and CI models*

The open shell molecules, with even number of electrons, have π^2 or π_g^2 ground-state electronic configuration. Several homonuclear diatomic molecules like O_2, S_2 and B_2 have π_g^2 ground state in the $D_{\infty h}$ point group which is reduced to the D_{2h} point group when the symmetry is lowered. Various heteronuclear diatomic radicals like PH, NH and SO have π^2 ground state in the $C_{\infty v}$ point group which is reduced to the C_{2v} point group when the symmetry is lowered. We have computed and presented here the rate coefficient of these open shell molecules (O_2, S_2, B_2) and radicals (PH, NH, SO) from the results of our previous studies. The rate coefficients for elastic and electron-excited processes are studied over a wide electron temperature range. We used a double zeta plus polarization (DZP) Gaussian basis set.

In our static exchange (SE) model, we first performed an SCF calculation for the ground state of the molecule with the chosen DZP basis set and obtained a set of occupied and virtual set of orbitals. In our limited CI model, we keep some electrons frozen in lower orbitals and allow the remaining electrons to move freely in the rest of the available molecular orbitals. In these open shell molecules, correlations lower the energies and dipole moment due to the large Hilbert space available with respect to HF-SCF calculations.

Many molecules with even number of electrons belong to open shell system due to π^2 or π_g^2 ground-state electronic configuration. This configuration gives rise to three low-lying states $X^3\Sigma_g^-$, $a^1\Delta_g$ and $b^1\Sigma_g^+$ in homonuclear diatomic molecules (O_2, S_2, B_2) and $X^3\Sigma^-$, $a^1\Delta$ and $b^1\Sigma^+$ in heteronuclear diatomic radicals (PH, NH, SO). We first performed an SCF calculation for the ground state of the molecule with the chosen DZP basis set and obtained a set of occupied and virtual set of orbitals.

In figures 1a and 1b we have shown the rate coefficients of O_2 molecule for elastic and inelastic cross-sections from the ground state to the three physical states. The threshold value for O_2 molecule is 13.94 eV.

In figures 2a and 2b we have shown the rate coefficients of the B_2 molecule for elastic and inelastic cross-sections from the ground state to the four physical states. The threshold value for the B_2 molecule is 9.54 eV.

In figures 3a and 3b we have shown the rate coefficients of the S_2 molecule for elastic and inelastic cross-sections from the ground state to the three physical states. The threshold value for the S_2 molecule is 10.02 eV.

In figures 4a and 4b we have shown the rate coefficients of the NH radical for elastic and inelastic cross-sections from the ground state to the three physical states. The threshold value for the NH radical is 14.56 eV.

In figures 5a and 5b we have shown the rate coefficients of the SO radical for elastic and inelastic cross-sections from the ground state to the four physical states. The threshold value for the SO radical is 11.12 eV.

In figures 6a and 6b we have shown the rate coefficients of the PH radical for elastic and inelastic cross-sections from the ground state to the three physical states. The threshold value for the PH radical is 10.26 eV.

4. Conclusions

We have computed and presented here the rate coefficient of open shell molecules (O_2, S_2, B_2) and radicals (PH, NH, SO) from the results of our previous studies. The rate coefficients for elastic and electron-excited processes are studied over a wide electron temperature range. We hope that the results presented here will not only be useful for comparison with future experimental studies but will also provide useful data in plasma modelling.

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